Use of ^{234}U and ^{238}U isotopes to evaluate contamination of near-surface groundwater with uranium-mill effluent: a case study in south-central Colorado, U.S.A.

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Abstract The ^{234}U/^{238}U alpha activity ratio (*AR*) was determined in 47 samples of variably uraniferous groundwater from the vicinity of a uranium mill near Cañon City, Colorado. The results illustrate that uranium isotopes can be used to determine the distribution of uranium contamination in groundwater and to indicate processes such as mixing and chemical precipitation that affect uranium concentrations. Highly to moderately contaminated groundwater samples collected from the mill site and land immediately downgradient from the mill site contain more than 100 μg/l of dissolved uranium and typically have *AR* values in the narrow range of 1.0–1.06. Other samples from the shallow alluvial aquifer farther downgradient from the mill contain 10–100 μg/l uranium and plot along a broad trend of increasing *AR* (1.06–1.46) with decreasing uranium concentration. The results are consistent with mixing of liquid mill waste (*AR* ≈ 1.0) with alluvial groundwater of small, but variable, uranium concentrations and *AR* of 1.3–1.5. In the alluvial aquifer, the spatial distribution of wells with *AR* values less than 1.3 is consistent with previous estimates of the probable distribution of contamination, based on water chemistry and hydrology. Wells more distant from the area of probable contamination have *AR* values that are consistently greater than 1.3 and are indicative of little or no contamination. The methodology of this study can be extended usefully to similar sites of uranium mining, milling, or processing provided that local geohydrologic settings promote uranium mobility and that introduced uranium contamination is isotopically distinct from that of local groundwater.

Key words Uranium isotopes · Uranium mill wastes · Uranium contamination

Introduction

The general decline of the uranium industry within the last decade has caused the closure of most conventional uranium mills in the United States and the implementation of site-specific decommissioning plans for remediation (U.S. Department of Energy 1995). Two important goals of mill site reclamation are the restoration of groundwater quality and the containment of contaminated groundwater on the mill site. The U.S. Environmental Protection Agency (USEPA) (U.S. Environmental Protection Agency 1987) has proposed specific goals for groundwater quality by defining maximum allowable concentrations of toxic contaminants at boundaries of inactive uranium-mill tailings sites.

Dissolved uranium is an obvious and universally measured indicator of groundwater contamination from uranium mining and milling activities, but the isotopic composition of dissolved uranium is less commonly determined (Still 1977; Airey 1986; Longsworth 1994). This study illustrates the use of ^{234}U/^{238}U isotopic ratios to investigate the spatial distribution of uranium contamination and to elucidate processes such as mixing or precipitation that determine the ultimate fate of introduced uranium. Such information is particularly helpful if contaminant plumes extend beyond site boundaries and if liability for environmental degradation must be established (Landa and Gray 1995).

Previous applications of ^{234}U/^{238}U ratios to trace isotopically distinct groundwater or to estimate mixing proportions of groundwater have focused on understanding natural hydrologic systems rather than contaminant migration (reviews in Osmond and Cowart 1976, 1992). In one recent study, however, Wirt (1993) successfully used ^{234}U/^{238}U ratios, in combination with uranium concentrations

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and stable isotopes, to identify groundwater contamination from uranium mine-dewatering releases.

This case study expands upon Wirt's (1993) study by measuring and interpreting $^{234}U/^{238}U$ ratios in variably contaminated water at a uranium-mill site. The uranium-isotope data are evaluated in conjunction with chemical data and well-site locations to provide further insights regarding the transport of contaminated waters and the mixing of contaminated water and natural groundwater. The methodology of this study should find useful application at similar sites where isotopically distinct liquid waste from uranium mines, mills, or uranium-processing plants has contaminated local groundwater.

Description of the study area

The study area consists of a uranium-mill site and adjacent downgradient area potentially affected by mill effluent. The mill is owned by the Cotter Corporation[1] and is located at an elevation of 1707 m (5600 ft) in the upper reaches of the Sand Creek drainage, approximately 1.6 km east of the Wet Mountains and approximately 3.2 km south of Cañon City, Colorado. Lincoln Park (population 5000) is located north of the mill site and south of the Arkansas River (Fig. 1). The study area was chosen because of the extensive record of local water-quality data extending from 1962, the existing network of wells available for groundwater sampling, the previously documented contamination of groundwater on and near the mill site, and the need to further evaluate contamination of groundwater in the populated areas of nearby Lincoln Park.

The mill began operation in 1958 and throughout its history received uranium ore primarily from mines in Colorado and Utah. Process water was piped from the Arkansas River. Original facilities included an alkaline-leach mill and unlined tailings ponds. In 1979 a sulfuric-acid-leach mill and a large, lined tailings-impoundment area were added. Operation of the alkaline-leach mill ceased in 1982, and all mill waste from the unlined ponds was transferred to the lined impoundment by 1983. The remaining acid-leach mill has been in standby mode since 1985.

Liquid waste (raffinate) and tailings solids produced during the mill operations were initially stored in unlined tailings ponds and later in the lined tailings-impoundment area. Seepage from the unlined tailings ponds and leaching of raffinate-deposited minerals in the unsaturated zone are the principal processes that caused documented contamination of shallow groundwater at the mill site (Wahler and Associates unpublished report 1978) and in some wells completed in the alluvial aquifer in adjacent Lincoln Park (Hearne and Litke 1987). Strongly raffi-

[1] The use of trade, product, industry, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

nate-affected water collected from the mill site is characterized by a predominance of sodium and sulfate ions, large values of specific conductance (4000–25 000 μS/cm), and large concentrations of dissolved uranium (2000–89 000 μg/l), molybdenum (5000–84 000 μg/l), and selenium (81–130 μg/l) (Hearne and Litke 1987; this study). Partly because of elevated concentrations of these constituents in some off-site well water in Lincoln Park, the USEPA added the Lincoln Park site to the Superfund National Priority List in 1984 (U.S. Environmental Protection Agency 1984).

Geology of the study area

The mill is located in a structural basin in the Sand Creek drainage (Fig. 1). The mill straddles the axis of the Chandler Syncline. This local basin is part of a larger structural basin, the Cañon City Embayment, that separates the Wet Mountains to the south of the embayment from the Front Range to the north.

The bedrock geology of the study area (Fig. 1) was mapped by Hershey (unpublished report) and Scott (1977). A highly generalized stratigraphic section of the study area is shown in Fig. 2. The mill site is underlain by as much as 256 m of claystones, siltstones, sandstones, and fluvial conglomerate of the Poison Canyon Formation of Paleocene age. Lithologic units of the Poison Canyon Formation near the mill site are characterized by extreme variability in thickness and lateral extent. The Raton Formation of early Tertiary and Late Cretaceous age underlies the Poison Canyon Formation and consists of as much as 152 m of medium- to coarse-grained, massive, nonmarine sandstone with thin interbeds of carbonaceous material in its upper part. The Vermejo Formation of Late Cretaceous age consists of as much as 230 m of fine- to medium-grained marine and nonmarine sandstones with interbedded sandy shales, carbonaceous shales, and bituminous coal seams. Formations of Late Cretaceous age beneath the Vermejo Formation include the Trinidad Sandstone, a fine- to medium-grained, massive to thin-bedded marine sandstone as much as 27 m thick, and the Pierre Shale, a clayey, silty, sandy marine shale with bentonite interbeds as much as 1170 m thick.

Surficial terrace deposits of Quaternary age in the study area generally are 6–18 m thick and range from bouldery, cobbly gravel to pebbly sand, silt, and clay. One such terrace deposit adjacent to the Arkansas River (Louviers Alluvium) underlies most of the flat-lying land of Lincoln Park (Scott 1977).

Hydrology of the study area

Surface drainage at the mill site is along Sand Creek, an 8-km-long ephemeral stream that is a tributary of the Arkansas River (Fig. 1). Sand Creek originates in the nearby foothills of the Wet Mountains and after crossing the mill site continues northeastward through Lincoln Park to join the river. Surface flow in all but the lowermost 1 km of Sand Creek is restricted to periods of heavy precipitation. In 1971, the U.S. Soil Conservation Service (SCS; now the Natural Resources Conservation Service) con-

Quaternary alluvium (Holocene)

Quaternary terrace alluvium (Holocene and Pleistocene)

Quaternary terrace alluvium (Pleistocene)

Tertiary Poison Canyon Formation

Tertiary and Cretaceous Raton Formation

Cretaceous Vermejo Formation

Cretaceous Trinidad Sandstone

Cretaceous Pierre Shale

Cretaceous Niobrara Formation, Carlile Shale, Greenhorn Limestone, Graneros Shale, Dakota Sandstone, and Purgatoire Formation, undifferentiated.

Jurassic Morrison and Ralston Creek Formations

Precambrian migmatitic biotite gneiss

——— Contact

▬▬▬ Fault

Base from U.S. Geological Survey 1:24,000 scale map State Plane Coordinate System Zone 3476

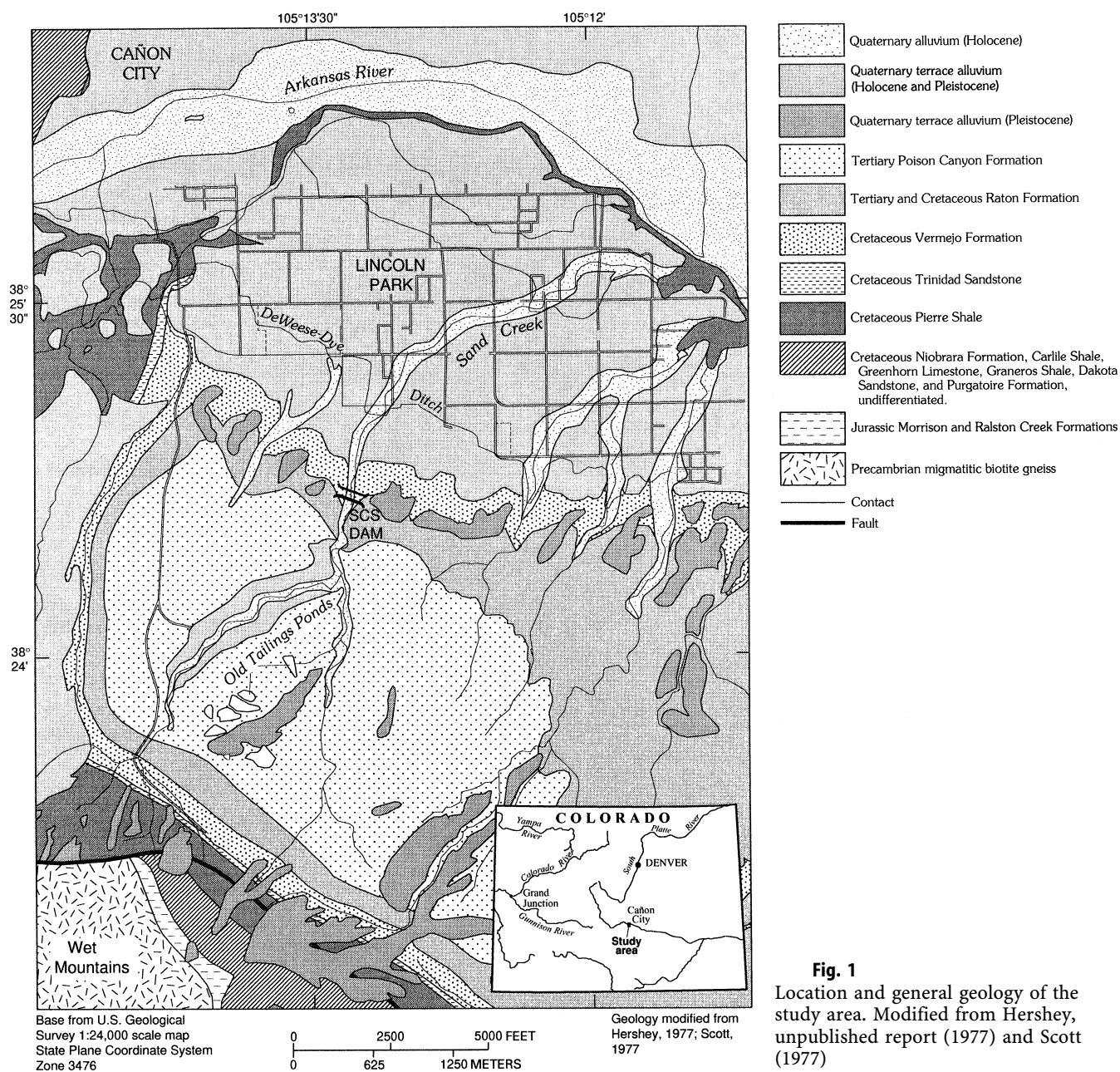Geology modified from Hershey, 1977; Scott, 1977

Fig. 1
Location and general geology of the study area. Modified from Hershey, unpublished report (1977) and Scott (1977)

structed a flood-control dam along Sand Creek that effectively collects all surface runoff from the mill site. The SCS dam is located at a gap in a low ridge of resistant sandstone of the Raton Formation (Fig. 1). In 1988, a clay barrier was installed along the south side of the SCS dam to serve as a hydraulic barrier to flow of alluvial groundwater from the site.

Shallow groundwater in the Sand Creek basin flows in a north-northeast direction across the mill site and Lincoln Park (Hearne ard Litke 1987). On the mill site, the uppermost water-yielding materials are in the Poison Canyon Formation or the alluvium along Sand Creek. Lithologic heterogeneity and highly variable fracture density within the Poison Canyon Formation cause large variation in measured hydraulic conductivity (Brown, unpublished re-

port 1993) and promote storage of water in perched lenses. In the Lincoln Park area the principal shallow aquifer is unconfined and hosted by highly permeable (10^{-1} to 10^{-3} cm/s) alluvial-terrace deposits of Quaternary age and underlying portions of weathered and fractured bedrock. The saturated parts of these units are collectively termed the 'alluvial aquifer' (Hearne and Litke 1987). A major control on the degree of saturation of the alluvial aquifer is the availability of water from the De-Weese-Dye Ditch (Fig. 1) and associated irrigation. This irrigation ditch carries water southeast across Lincoln Park and irrigates land located between the ditch and the Arkansas River (Fig. 1). During the irrigation season of April to October, leakage from the ditch and recharge from applied irrigation water produce seasonally variable
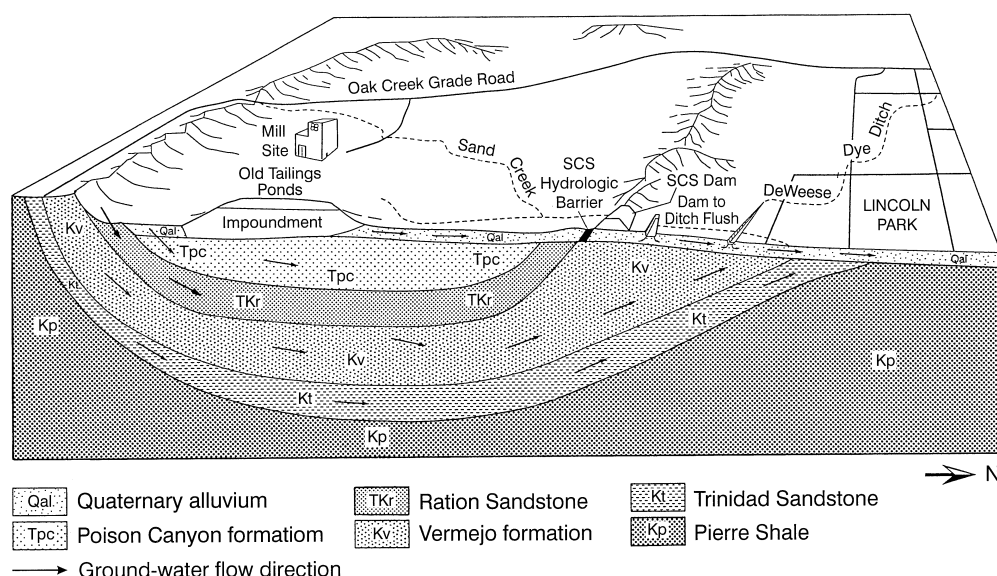
Fig. 2
Generalized stratigraphic section and surficial features of the study area. Modified from Colorado Department of Health (unpublished report 1993)

saturation of the alluvial aquifer near and north of the ditch.

Hearne and Litke (1987) used chemical, stable isotopic, and hydrologic data from wells on the mill site and in the Lincoln Park area to conclude that raffinate-affected groundwater entered Lincoln Park predominantly through shallow migration pathways. These preferred pathways include alluvium along Sand Creek and possibly include alluvium-filled channels on the weathered bedrock underlying the southern part of Lincoln Park. They also concluded that the geochemistry of contaminated water was consistent with mixing of raffinate with native groundwater from the Poison Canyon Formation and the alluvial aquifer. Uranium, molybdenum, and selenium are soluble constituents of raffinate that are particularly diagnostic of raffinate-affected water.

Criteria for applying $^{234}U/^{238}U$ isotopic measurements

Successful application of $^{234}U/^{238}U$ ratios for tracing uraniferous contaminant plumes and modeling their mixture with native groundwater requires an isotopic distinction between contaminant and natural groundwater and a generally oxidizing environment in which uranium is highly mobile and largely conserved in solution. Presently understood mechanisms for fractionating ^{238}U (half-life $= 4.47 \times 10^9$ years) from its radioactive daughter product ^{234}U (half-life $= 2.44 \times 10^5$ years) allow some theoretical basis for predicting distinctly different isotopic compositions for uranium in mill raffinate and native groundwater. Uranium ores that have not been subject to major oxidative leaching within the last million years approximate closed systems that are in radioactive (secular) equilibrium. In secular equilibrium, the rate of decay of ^{234}U is equal to the rate of decay of ^{238}U parent. If chemically separated uranium isotopes are measured in terms

of their alpha-emission rates, radioactive equilibrium between ^{238}U and ^{234}U represents a condition of equal alpha activity and a $^{234}U/^{238}U$ alpha activity ratio (*AR*) of 1.0. High-grade uranium ores that have a more recent history of open-system alteration are a mixture of materials with $AR > 1.0$ and $AR < 1.0$ (Cowart and Osmond 1977). Considering the variety of uranium ores received during the operation of the mill, a time-integrated average uranium-isotope composition of an *AR* of 1.0 ± 0.1 is estimated.

Raffinate contains residual amounts of uranium originally brought into solution by aggressive attack of uranium ore by strong oxidizing solutions of acid or alkali. Rapid, nearly complete dissolution of uranium from finely crushed ore samples should not promote isotopic fractionation. Likewise, further chemical processing of the leachate to efficiently remove most uranium from solution by solvent exchange, sorption, or precipitation fails to substantially fractionate U isotopes. Thus, raffinate should retain the uranium-isotope composition of the processed ore sample.

In contrast, most natural groundwater has a $^{234}U/^{238}U$ alpha activity ratio > 1.0 (Osmond and Cowart 1976). Typical *AR* values for groundwater fall in the range of 1–3, but values in excess of 10 have been reported (Cherdyntsev 1971; Kronfeld 1974; Szabo 1982). Dissolved ^{234}U is present in excess because of isotopic fractionation that occurs at the mineral/water interface during prolonged, mild leaching of uranium by groundwater. Mechanisms for the preferential leaching of ^{234}U are related to its origin by radioactive decay (Osmond and Ivanovich 1992). Fractionation results from alpha-recoil displacement of a ^{234}U atom from the site of its parent ^{238}U atom. This recoil displacement can be across the mineral-solution interface or into other crystal domains that become more leachable because of the damage caused by recoil of the ^{234}U atom.

Conditions that favor uranium mobility occur in aquifer environments that promote the formation of highly sol-

uble oxidized U(VI) species. Optimal environments are near-surface, unconfined aquifers that are open to exchange with the atmosphere and that contain sparse organic matter. Optimal chemical characteristics include measurable concentrations of dissolved oxygen and dissolved carbonate, the latter to stabilize uranium in oxidizing solution by the formation of uranyl carbonate species (Langmuir 1978). Relatively mobile uranium is indicated by positive correlation with conservative constituents such as chloride. Existing water-quality information for the study area and data presented in this study indicate an environment that generally favors transport of dissolved uranium, although sorption onto mineral surfaces (especially iron and manganese oxyhydroxides) retards migration of dissolved uranium and precludes strictly conservative behavior.

Sampling and analytical methods

Forty-four wells, one spring, two subsurface drains, and two surface-water sites were sampled for this study. The majority of samples (36) were collected from January to March 1995, and these samples were supplemented with a second collection in June and July 1995 (Table 1). Wells and subsurface drains were chosen to provide: (1) good areal coverage within the mill site and along the drainage of Sand Creek into Lincoln Park; (2) major emphasis on wells producing from shallow depths (< 30 m) in the Poison Canyon Formation and the alluvial aquifer; and (3) a large range of concentrations of dissolved uranium and molybdenum, based on data from previous sampling. The large range of concentrations was bounded by end-member samples representing highly raffinate-affected water from the mill site and probable uncontaminated alluvial water from three wells located substantial distances from the previously estimated path of the raffinate plume (Environ Corporation and others unpublished report 1991). Surface-water samples included irrigation water from the DeWeese-Dye Ditch and treated municipal water from the Arkansas River. The latter was used by Cotter Corporation from 1990 to 1995 to flush uranium and molybdenum from the alluvium between the SCS dam and the DeWeese-Dye Ditch. Most wells were sampled with portable submersible pumps, but some domestic wells in Lincoln Park were sampled using existing submersible pumps. Most wells were purged and samples taken after on-site measurements of temperature, specific conductance, pH, and dissolved-oxygen concentration in the discharge water were stable for a period of at least 10 minutes. Sample water was filtered at the time of collection through disposable filters with 0.45-μm openings into acid-rinsed polyethylene bottles and then was acidified to pH < 2 with ultrapure nitric acid.

Upon receipt at the laboratory, each sample was analyzed for concentrations of dissolved uranium and molybdenum by inductively coupled plasma-mass spectrometry (ICP-MS). Reported detection limits were 0.1 and 1.0 μg/l, respectively. Estimated precision of the technique is $\pm 10\%$ (relative standard deviation) for the concentration levels of most samples. Additional aliquots of 42 samples were submitted for determination of uranium-isotope compositions and for confirmation of uranium concentrations by radioisotope-dilution alpha spectrometry (Rosholt 1984). A spike of ^{236}U was added to each sample and the sample evaporated to dryness. The residue was dissolved in acid and processed with a series of anion-exchange resins to generate a pure separate of uranium. Dissolved uranium was then electro-deposited as a thin film on a stainless-steel planchet for alpha counting. A minimum of 10 000 counts was accumulated at each alpha-energy peak of interest. Precision of the reported ^{234}U/^{238}U alpha activity ratio (AR) is better than $\pm 2\%$ (relative standard deviation) and AR values are based on results of two separate counting periods. Uranium concentrations determined by both methods generally were indistinguishable within the limits of combined analytical precision. Results for ICP-MS are reported herein to facilitate comparison with molybdenum concentrations determined by the same method.

Results and discussion

Chemical data

Uranium and molybdenum concentrations for samples collected from the study area vary over large concentration ranges of < 0.1–89 000 μg/l and < 1.0–84 000 μg/l, respectively (Table 1). The largest concentrations for both metals were from site 701 (Fig. 3), a sump approximately 6 m deep at the terminus of a gravel-filled trench that collects raffinate-affected groundwater from the vicinity of the old, unlined ponds. Additional sites (333, 312, 313, 330, 138) with unusually large concentrations of uranium (> 500 μg/l) and molybdenum (> 5000 μg/l) were located immediately downgradient from the mill site along the Sand Creek drainage (Fig. 3). Uranium and molybdenum concentrations of several hundred micrograms per liter and higher are clearly anomalous compared to natural groundwater and surface water which, except in mineralized areas, rarely contain more than 100 μ/l of either element (Fix 1956; Kaback and Runnells 1980).

The other extreme of the concentration range includes three sites (10, 11, 114) located north and east of Lincoln Park, at substantial lateral distances from the probable path of the raffinate plume, which is approximately along the axis of Sand Creek (Fig. 3). Based on location and the availability of historical records of water composition at these three sites, they were chosen to provide estimates of background compositions in the alluvial aquifer. A statistical summary of historical uranium and molybdenum concentrations at these background sites is presented in Table 2. Uranium concentrations range from 4 to 31 μg/l and molybdenum concentrations range from < 5 to 40 μ/l. If a concentration of dissolved molybdenum in excess of 40 μg/l is used as an indicator of raffinate-affected water, contamination has migrated along a broad

Table 1

Uranium isotope composition, uranium and molybdenum concentrations, and on-site measurements (Geohydrologic units: *Qt* terrace deposits of Quaternary age, *Tpc* Poison Canyon Formation of Tertiary age, *TKr* Raton Formation of Tertiary and Cretaceous age, *Kv* Vermejo Formation of Cretaceous age) *n.d.* not determined

Site number (See Fig. 3)	Well depth (m)	Formation in which completed	Month sampled (in 1995)	$^{234}U/^{238}U$ alpha activity ratio	Uranium (μg/l)	Molybdenum (μg/l)	Dissolved oxygen (mg/l)	Specific conductance (μS/cm)	pH
				Water wells and spring					
10	13.1	Qt	March	1.33	24	8.7	5.6	850	7.1
11	13.7	Qt	March	1.41	31	5.8	5.7	2260	7.4
19	12.8	Qt	March	1.29	72	550	5.0	931	7.1
20	11.6	Qt	March	1.26	35	140	4.2	685	7.4
114	18.3	Qt	March	1.32	8.7	6.0	4.6	537	7.3
117	24.2	Qt	July	1.23	34	240	9.5	585	7.2
119	12.2	Qt	March	1.09	140	1800	6.3	723	7.4
120	7.9	Qt	July	1.22	14	150	9.0	621	7.4
122	24.4	Qt	July	1.12	57	400	8.3	616	7.3
123	14.0	Qt	March	1.22	83	620	4.8	1005	7.1
124	21.9	Qt	March	1.14	47	250	5.7	569	7.2
129	15.8	Qt	March	1.17	55	150	7.2	614	7.1
130	18.3	Qt	March	1.33	18	45	5.1	676	7.2
138	14.6	Qt	March	1.06	570	5200	6.8	2200	6.8
144	14.0	Qt	March	1.23	40	150	5.0	821	7.0
163	37.5	Qt and Kv	March	1.40	5.5	2.0	3.5	1730	7.7
165	Spring	Qt	July	1.38	3.9	22	4.8	382	7.3
166	12.2	Qt	July	1.35	13	66	7.0	494	7.2
167	n.d.	Qt	July	1.31	9.6	36	8.8	550	7.4
173	18.3	Qt	July	1.26	25	100	7.1	630	7.1
174	16.9	Qt	July	1.38	14	42	9.0	567	7.2
190	12.2	Qt	March	1.16	39	420	1.0	552	7.2
197	19.8	Qt	March	1.38	16	6.5	5.6	681	7.1
228	39.3	Qt and Kv	March	1.42	23	20	4.8	824	7.4
230	14.6	Qt	July	1.38	16	13	10.0	602	7.2
330	11.9	Qt	June	1.06	1900	9600	6.2	3980	7.4
2107	16.8	Qt	July	1.46	11	4.6	5.3	618	7.2
1	15.8	Tpc	March	1.20	0.2	<1.0	2.5	3000	5.8
14	30.5	Tpc	February	n.d.	0.39	6.1	<0.1	2820	8.1
17	45.1	Tpc	February	n.d.	0.62	2.0	<0.1	978	8.3
22	30.5	Tpc	January	n.d.	1.4	3.0	0.3	1080	9.6
312	10.7	Tpc	March	1.02	2000	9800	6.6	3270	7.9
313	14.9	Tpc	February	n.d.	3600	20000	4.0	5100	7.7
324	106.7	Tpc	February	1.75	0.46	4.4	<0.1	979	7.5
325	24.7	Tpc	March	2.49	3.3	3.0	1.3	3260	7.0
333	18.3	Tpc	March	1.05	3700	6900	n.d.	4330	7.2
336	36.6	Tpc	March	1.50	130	43	1.7	2400	7.3
350	9.1	Tpc	February	1.14	3.1	640	<0.6	2800	7.4
357	11.3	Tpc	March	3.43	9.1	21	1.1	2790	7.2
806	22.9	Tpc	February	2.31	25	3.7	4.1	3850	6.3
327	64.0	Kv	February	1.09	1.2	150	<0.1	1475	8.1
328	114.3	Kv	March	1.09	1.0	59	n.d.	1026	9.4
339	322.5	Kv	January	n.d.	<0.1	<1.0	<0.2	11700	5.5
342	38.1	Kv	February	1.61	3.9	2.0	0.5	2570	6.7
335	67.1	TKr	February	n.d.	0.89	3.9	<0.1	2520	6.7
				Surface water					
526	0	DeWeese-Dye Ditch	June	1.77	2.5	1.2	8.5	326	8.5
997	0	Municipal water	June	1.54	1.2	2.4	8.3	232	7.4
				Subsurface drains					
701	6	Pond 1 trench	March	0.98	89000	84000	n.d.	25400	7.4
710	7	Toedrain	March	1.19	890	550	0.9	6820	7.0
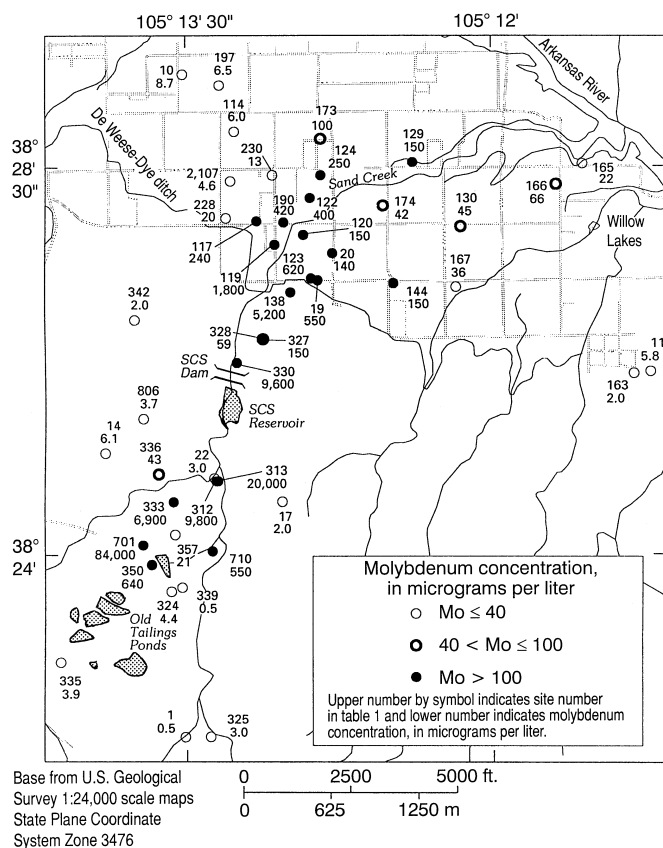
Fig. 3
Location of groundwater sampling sites and concentrations of dissolved molybdenum
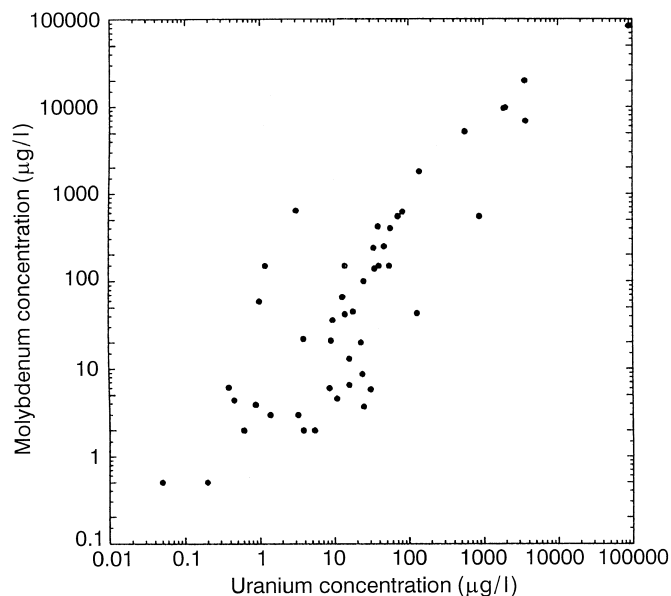

Fig. 4
Relation of uranium concentrations to molybdenum concentrations for groundwater and surface-water samples. Molybdenum and uranium concentrations less than the detection limit are assumed to equal one-half of the detection limit

front to the north-northeast and east-northeast from the SCS dam and has almost reached the Arkansas River (Fig. 3). A log-log plot of uranium and molybdenum concentrations for the samples listed in Table 1 is shown in Fig. 4. A strong positive correlation (parametric correlation coefficient = 0.97) is indicated between the two constituents. A similar strong correlation ($r = 0.89$) between

uranium and molybdenum was reported by Hearne and Litke (1987). Three notable outliers to this trend (sites 327, 328, 350) have anomalously small uranium concentrations compared to molybdenum concentrations (Table 1, Fig. 4). All three samples are from wells completed in bedrock units (Poison Canyon and Vermejo Formations), which contain reductants such as interbedded carbonaceous matter, coal seams, and disseminated sulfides. Preferential reduction of uranium to the relatively insoluble U(IV) species is a possible mechanism for producing separation of dissolved uranium and molybdenum. This process is illustrated in some roll-front uranium deposits where groundwater flow across a redox gradient has pro-

Table 2
Summary statistics for uranium and molybdenum concentrations in background alluvial wells

Site number (See Fig. 3)	Sampling period	U or Mo	No. of determinations	Concentration (µg/l)				
				Mean	Standard deviation	Median	Minimum	Maximum
10	2/89–3/95	U	31	17.3	±5.4	18	6	30
		Mo	27[b]	7.1	±2.1	7	<5	11
11	2/89–3/95	U	32	15.5	±7.4	18	5	31
		Mo	25[b]	9.5	±6.2	8	<5	30
114	8/84[a]–3/95	U	68	11.8	±3.4	11	4	24
		Mo	52[b]	8.3	±6.1	7	<5	40

[a] Prior data for well 114 were not included because of unsuitably large detection limits
[b] Number indicates number of determinations exceeding the detection limit of 5 µg/l. A value of 0.7 of the detection limit

(3.5 µg/l) was assigned to determinations below detection limit when calculating mean and standard deviation of Mo. Total number of determinations were the same as for uranium and were used to calculate medians

duced highly localized precipitation of uranium and more diffuse, downgradient precipitation of molybdenum (Harshman 1974). Two of the three samples have unusually low concentrations of dissolved oxygen (<0.6 mg/l), consistent with an increased abundance of reductants in the aquifer. Excluding these three samples, the log-log plot shows the greatest scatter where uranium and molybdenum concentrations are less than about 40 μg/l. Most of this scatter is likely caused by variability of background concentrations of uranium and molybdenum in the alluvial aquifer and bedrock aquifers.

The relations of uranium and molybdenum concentrations to specific conductance (Fig. 5A, B) show no overall trends. However, if samples with less than 40 μg/l of uranium and molybdenum were excluded, the plots would show positive correlations that probably indicate initial, downgradient dilution of raffinate from site 701 with local groundwater. Samples with uranium and molybdenum concentrations less than 40 μg/l and specific-conductance values greater than or equal to 1000 μS/cm do not fit the trends and generally indicate variable background concentrations of uranium and molybdenum in the Vermejo, Poison Canyon, and Raton Formations. Samples from sites 327, 328, and 350 additionally deviate

from the trend because of selective precipitation of raffinate-derived uranium, as previously described.

Water from the alluvial aquifer, which has specific-conductance values generally less than 1000 μS/cm (Table 1), is fresher than water from bedrock aquifers. This condition is due to the greater permeability of alluvium, which favors more rapid flushing with relatively fresh recharge water from headland areas and from irrigation ditches. Water from the alluvial aquifer also displays a smaller range of pH (6.8–7.7) than water from bedrock aquifers (5.8–9.6). This smaller range indicates less variable geochemical environments in alluvium compared to bedrock. Dissolved-oxygen concentrations (Table 1) indicate that alluvial groundwater is generally well oxygenated, with concentrations generally exceeding 4 mg/l. The oxidizing environment favors formation of highly soluble species of uranium (VI) and molybdenum (VI). Consistently detectable dissolved-oxygen concentrations satisfy the previously discussed requirement of an environment that promotes uranium solubility and mobility. In contrast, dissolved-oxygen concentrations for water samples from the bedrock aquifers range from undetectable (less than 0.2 mg/l) to large (6.6 mg/l). Groundwater samples with less than 0.6 mg/l dissolved oxygen have concentrations of dissolved uranium less than 4 μg/l (Table 1, Fig. 6A);
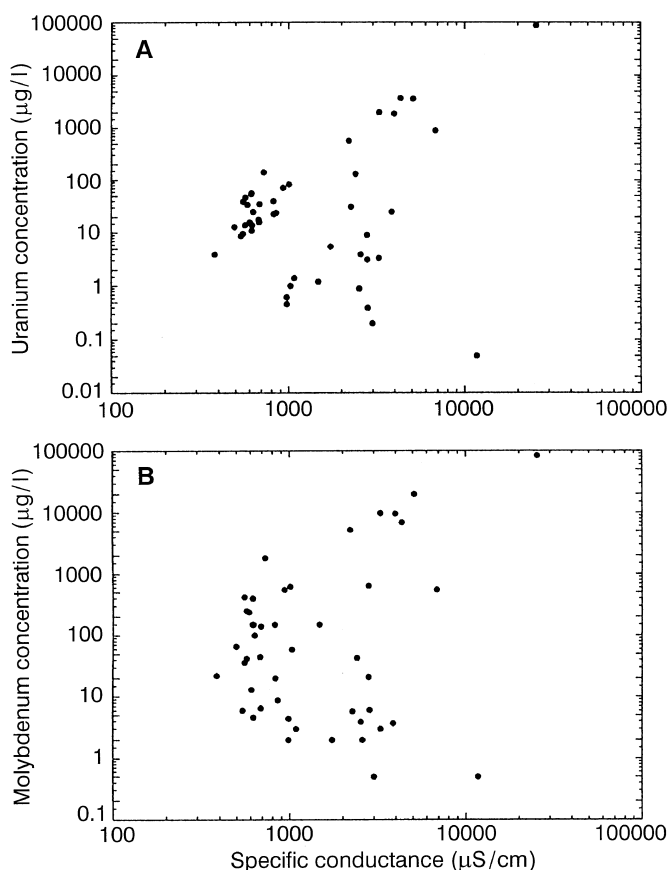

Fig. 5
Relation of (A) uranium and (B) molybdenum concentrations to specific conductance for groundwater samples. Molybdenum and uranium concentrations less than the detection limit are assumed to equal one-half of the detection limit
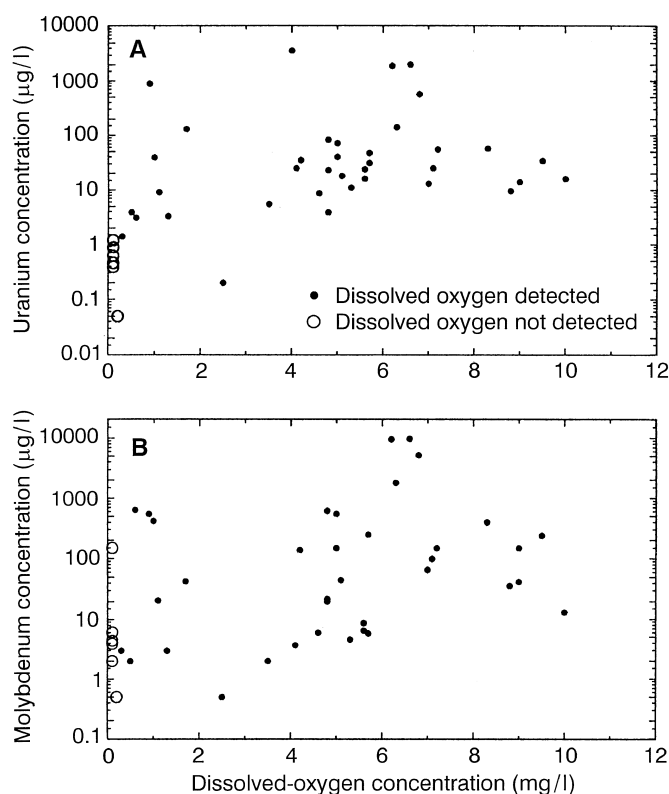

Fig. 6
Relation of (A) uranium and (B) molybdenum concentrations to dissolved-oxygen concentrations for groundwater samples. Molybdenum and uranium concentrations less than the detection limit are assumed to equal one-half of the detection limit

whereas, the same samples have concentrations of molybdenum that range from <1.0 to 640 μg/l (Table 1, Fig. 6B). These results demonstrate that in some moderately reducing environments molybdenum is substantially more soluble, and thus more mobile, than uranium.

Uranium isotopic data

AR values of $^{234}U/^{238}U$ in water samples range from 0.98 to 3.43 (Table 1). Samples from the alluvial aquifer fall within the range 1.06–1.46 whereas samples from the Vermejo, Poison Canyon, and Raton Formations fall in the broader range of 0.98–3.43. The three control samples representing raffinate uranium (sites 312, 333, and 701) had AR values ranging from 0.98 to 1.05. The three background samples from the alluvial aquifer (sites 10, 11, and 114) had AR values ranging from 1.32 to 1.41. The distinct difference in AR values of these two sets of control samples indicates that AR values can be used to trace migration and mixing of raffinate-affected water in the alluvial aquifer.

A plot of AR values relative to uranium concentrations (Fig. 7A) indicates that samples with uranium concentrations greater than 100 μg/l generally have AR values close to 1.0, indicating a raffinate source. All near-surface wells downgradient from site 701 to the DeWeese-Dye Ditch (sites 333, 312, 330, and 138) have AR values less than or equal to 1.06. A deeper well (site 336) with a uranium concentration of 130 μg/l has an unusually high AR of 1.50. This sample may contain substantial amounts of natural uranium leached from the host Poison Canyon Formation, which can yield AR values as high as 3.43 (Table 1). One subsurface drain sample (site 710) has a uranium concentration of 890 μg/l and is clearly contaminated with raffinate, but has a somewhat elevated AR of 1.19. This near-surface drain collects seepage from a limited volume of mill tailings, and the samples may not be as representative of integrated drainage as samples from wells located farther downgradient. Because these two samples (sites 336, 710) probably are not representative of raffinate that enters the alluvial aquifer, they are not discussed further.

Samples with uranium concentrations less than 100 μg/l have a wide range of AR values from 1.09 to 3.43 (Fig. 7A). The subset of samples from the Poison Canyon and Vermejo Formations span the range of AR values, and all samples with AR greater than 1.46 come from these formations (Table 1). In contrast, the subset of samples from the alluvial aquifer that contain less than 100 μg/l fall within a much more restricted range of AR of 1.12 to 1.46 (Table 1) and constitute a cluster of points on Fig. 7A that fall in the uranium concentration range of 10–100 μg/l. This cluster of points defines a trend in which AR values decrease with increasing uranium concentration and appear to approach a limiting raffinate-like value of AR ~ 1.0. This trend is consistent with a possible mixing relationship between background alluvial groundwater and raffinate.

A plot of AR values relative to molybdenum concentrations (Fig. 7B) illustrates relations similar to those shown
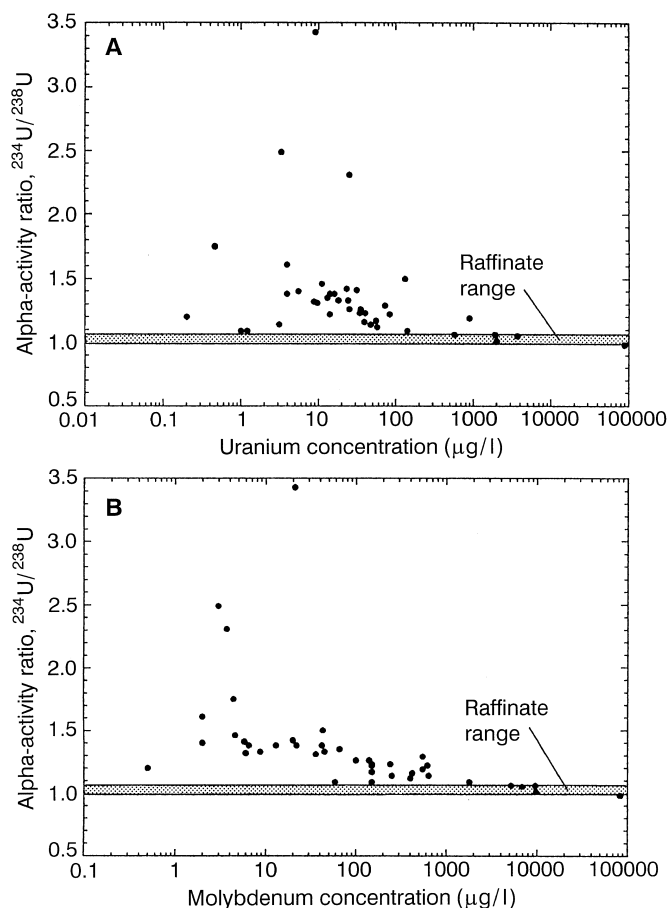

Fig. 7
Relations of $^{234}U/^{238}U$ alpha activity ratio to (A) uranium concentrations and (B) molybdenum concentrations for groundwater samples. A horizontal zone at AR ~ 1.0 indicates the proposed range for liquid mill waste (raffinate). Molybdenum concentrations less than the detection limit are assumed to equal one-half of the detection limit

by uranium concentrations. Samples with molybdenum concentrations greater than 700 μg/l exhibit AR values close to 1.0, and for these samples a raffinate source is indicated. Most of the samples containing 40–700 μg/l molybdenum are from the alluvial aquifer (Table 1) and fall along a negatively sloping trend that approaches AR values of 1.0 at high molybdenum concentrations.

Major sources of recharge to the alluvial aquifer are leakage from irrigation ditches and percolation of excess irrigation water. Uranium concentrations in the surface-water samples are 2.5 μg/l for site 526, from DeWeese-Dye Ditch, and 1.2 μg/l for site 997, which represents water injected downstream from the SCS dam. These uranium concentrations are small relative to concentrations in raffinate-affected groundwater or uncontaminated, resident (background) alluvial groundwater. As this dilute surface water recharges the alluvial aquifer, the uranium concentration and isotopic composition are modified in response to dissolution and steady-state exchange with a large reservoir of naturally occurring uranium present on

mineral surfaces. As a result, surface water recharged to the alluvial aquifer quickly assumes the *AR* of the background alluvial groundwater and does not complicate interpretations based on a well-defined background *AR*. Because substantial contribution of water to the alluvial aquifer from deeper bedrock aquifers is considered unlikely (Hearne and Litke 1987), groundwater data from the Vermejo and Poison Canyon Formations will not be discussed further.

Processes affecting uranium concentration and isotopic composition in the alluvial aquifer can be illustrated with a plot of activity ratio relative to the reciprocal of uranium concentration (Fig. 8). On this plot, horizontal displacement of points to the right indicates a decrease in uranium concentration in the absence of isotopic changes. Such decreases could result from the initial dilution of concentrated raffinate with local groundwater of relatively insignificant uranium concentration, or by chemical precipitation of uranium, or by sorption of uranium onto mineral surfaces. Apparent alignment of points along positive-sloped mixing lines anchored at one end by highly raffinate-affected samples (large uranium concentrations, *AR* near 1.0) indicates mixing of diluted raffinate with native alluvial groundwater of higher *AR* and lower uranium concentration. In this case, raffinate must be dilute enough that the uranium contributed by alluvial groundwater constitutes a substantial fraction of the total dissolved uranium in the mix.

In Fig. 8, the proposed range of background *AR* for alluvial groundwater is shown as 1.3–1.5. This selection is based on the measured values for postulated background wells 10, 114 (Banta 1994), and 11, and the measured values for seven other sites (163, 165, 167, 197, 228, 230, and 2107) that have molybdenum concentrations less than or equal to 40 μg/l, the previously estimated maximum background concentration. All sites with *AR* values less

than 1.3 have molybdenum concentrations greater than or equal to 100 μg/l and likely are more affected by raffinate. Three samples (sites 130, 166, and 174) have *AR* values that fall in the estimated background range but have molybdenum concentrations slightly greater than 40 μg/l (45, 66, and 42 μg/l, respectively). This suggests that molybdenum concentration may be a more sensitive indicator of minor raffinate contamination than uranium concentration or *AR*.

Background concentrations of uranium in alluvial groundwater can be estimated by noting in Fig. 8 the range of uranium concentrations for samples with *AR* values between 1.3 and 1.5 (Table 1, Fig. 8). This range of 3.9–31 μg/l is nearly identical to the range of 4–31 μg/l displayed in historical uranium concentration data from the three background wells (Table 2). A maximum range of background uranium concentrations also may be estimated by noting the intersections of the leftmost and rightmost of possible mixing lines with horizontal lines drawn at *AR* values of 1.3 and 1.5. This approach suggests a possible background uranium-concentration range of about 6–70 μg/l for the alluvial aquifer. The greatest uncertainty is in the maximum value because small horizontal displacements of points at the left side of the figure correspond to large differences in uranium concentration. Additional uncertainty is associated with the position of leftmost and rightmost apparent mixing lines. These lines are drawn through a few outlying points, which may be horizontally displaced on the uranium concentration axis by processes other than mixing; for example precipitation, sorption, dilution, and evaporative concentration. Most raffinate-affected samples plot near the middle mixing line and are encompassed by a tighter array of possible mixing lines defining alluvial aquifer end-member uranium concentrations of about 12–32 μg/l.
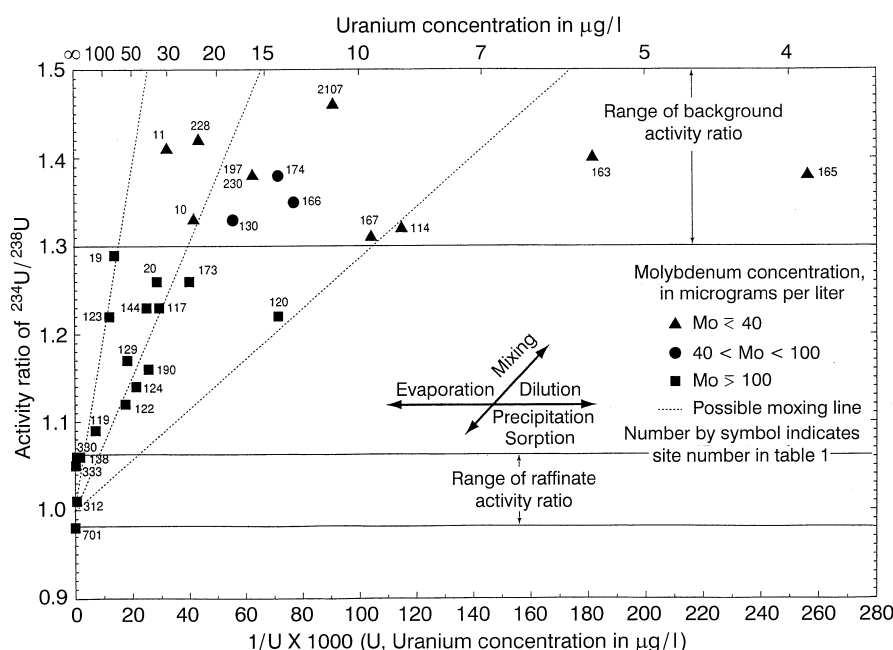

Fig. 8
Relation of $^{234}U/^{238}U$ alpha activity ratio to the reciprocal of uranium concentration for raffinate control samples and samples of alluvial groundwater. Samples are additionally coded according to their molybdenum concentrations

Alignment of several samples along an apparent mixing line is suggestive of a common mixing relation; but considering the widespread areal distribution of samples plotting near the middle mixing line shown in Fig. 8, the results are more generally interpreted to indicate a similar character of mixing in the alluvial aquifer that affects the composition of a population of samples. If mixing is considered exclusively it is possible to calculate mixing proportions for any sample that lies along an apparent mixing line connecting chosen end-members (Osmond and others 1974). If waters 1 and 2 produce a mixed water 'm' the operative equation for computing relative volumes is:

$$V_1/V_m = (S_1/S_m) \times (AR_2 - AR_m/AR_2 - AR_1) \tag{1}$$

Where S equals $1/U$, V is the volume, and AR is the $^{234}U/^{238}U$ alpha activity ratio.

According to Eq. 1 a mixture of dilute raffinate ($U = 100$ µg/l, $AR = 1.05$) and background alluvial groundwater ($U = 15$ µg/l, $AR = 1.5$) will lie outside of the field defining alluvial groundwater compositions ($AR_m < 1.3$) if the mix contains more than 9 volume percent of dilute raffinate. Smaller volumes of dilute raffinate are required if the alluvial groundwater end member has an AR closer to 1.3. Larger volumes of dilute raffinate end-member are required if it has a uranium concentration less than 100 µg/l, or an AR greater than 1.05.

An areal plot of AR values (Fig. 9) defines a plume of dissolved uranium with AR values less than 1.3. This plume originates in the vicinity of the old tailings ponds and extends northward through the gap in the ridge where the SCS dam is located and into the alluvial aquifer underlying Lincoln Park. The distribution of AR values in the Lincoln Park area indicates that the uranium plume appears to widen as it extends northward and northeastward from the vicinity of the SCS dam. Comparison of the distribution of AR values (Fig. 9) with that of molybdenum concentrations (Fig. 3) indicates a similar shape for the two indicated plumes. However, the molybdenum plume, as indicated by molybdenum concentrations greater than 40 µg/l, extends farther downgradient than the uranium plume, as indicated by AR values less than 1.3. This suggests that raffinate-derived uranium may be less mobile than molybdenum in the alluvial aquifer, despite the presence of abundant dissolved oxygen. Sorption of uranium and molybdenum by iron and manganese oxyhydroxides can occur under oxidizing conditions, and minor quantities of these phases are present in the alluvial aquifer. Alternatively, the large contrast between a molybdenum concentration of 40 µg/l and the mean molybdenum concentrations in the three alluvial background wells (<10 µg/l) may make molybdenum a more sensitive indicator of minor contamination than uranium concentration or AR.

Other applications

Other sites of uranium mining, milling, or processing are suitable for uranium isotopic study provided that mine drainage or liquid wastes have a distinctive $^{234}U/^{238}U$ isotopic signature. Aggressive leaching of uranium ore is required to generate $^{234}U/^{238}U$ alpha activity ratios of 1.0 ± 0.1 in solution that are lower than ratios that occur in most natural water. Aggressive leaching is most probable at mine sites where workings or mine wastes are subject to rapid oxidative weathering. If sulfides are present in ores or tailings piles, aggressive leaching is further aided and perhaps prolonged by local generation of acidic drainage. Industrial liquid wastes from uranium mills carry residual uranium originally derived from aggressive acid or alkaline attack of ores. Liquid wastes from uranium processing (nuclear fuel reprocessing or uranium metal fabrication) may carry residual uranium originally brought into acid solution during chemical processing or reprocessing of a variety of uranium-bearing materials. Such liquids should retain the uranium isotopic composition of the processed material. If ^{235}U-enriched or ^{235}U-depleted materials are processed, this could expand the scope of uranium isotopic studies to include measurements of distinctive $^{235}U/^{238}U$ ratios in contaminant plumes.

The uranium isotopic composition of leachate from old exposed tailing piles may be subject to temporal variation that could limit some applications. If original inter-
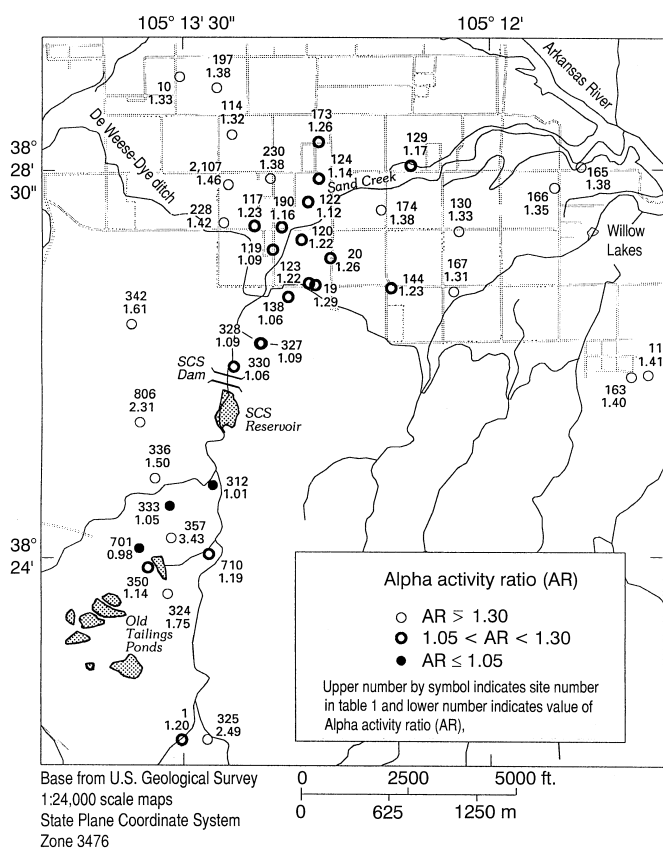

Fig. 9
$^{234}U/^{238}U$ alpha activity ratios for groundwater in 1995

stitial fluids composed of liquid mill waste and highly soluble salts are largely removed during prolonged leaching, the uranium isotopic composition of leachate could evolve from an initial *AR* of approximately 1.0 to higher values of *AR* more typical of runoff from naturally weathered uranium-bearing rock. This diminished isotopic contrast with local groundwater could limit the tracing of leachate that is recently added to local aquifers. Taking a different view, the uranium-isotopic composition of seepage could be used to monitor the extent of flushing of liquid mill waste from tailings and to document the approach to more natural, weathering-related leaching of the remaining solids.

Conclusions

The uranium isotopic composition (^{234}U/^{238}U) in near-surface groundwater near a uranium mill in Colorado indicates variable contamination with isotopically distinct mill-waste liquid (raffinate). The areal distribution of wells showing different isotopic compositions is consistent with previous interpretations of the distribution of contamination based on chemical measurements. The combination of uranium-isotope data with measurements of dissolved uranium concentrations provides an independent assessment of mixing of raffinate with alluvial water downgradient from the mill. The additional combination with measurements of dissolved molybdenum concentrations also suggests raffinate-derived molybdenum contamination of alluvial groundwater, including some wells in which precipitation or sorption of uranium probably occurred. Measurements of ^{234}U/^{238}U ratios can be a valuable supplement to integrated studies of contaminant migration at uranium mines or mill sites. Uranium isotopes offer the added potential for interpretation of processes such as mixing, precipitation, and sorption that can affect the distribution of uranium contamination. Application of uranium-isotope data is most successful in study areas that have isotopically distinct contamination, relatively simple hydrology, and oxygenated groundwater to promote uranium mobility.

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